Preparation of Mn-fiber standards for the efficiency calibration of the delayed coincidence counting system (RaDeCC)

Jan C. Scholten[1*], Mai Khanh Pham[1], Oxana Blinova[1], Matthew A. Charette[2], Henrieta Dulaiova[2,3], Mats Eriksson[1]

[1] International Atomic Energy Agency – Marine Environment Laboratories, Monaco
[2] Woods Hole Oceanographic Institution, Woods Hole, MA, USA
[3] present address: University of Hawaii, Honolulu, USA

* Corresponding author: Marine Environment Laboratories; 4, Quai Antoine 1er, 98000 Monaco, Tel.: 00377 9797 7228; Email: j.scholten@iaea.org

Abstract

Precise measurements of the short lived radium isotopes ^{223}Ra and ^{224}Ra by means of the delayed coincidence counting system (RaDeCC) rely on an efficiency calibration of this system using Mn-fiber standards for which radium activities are exactly known. We prepared seventeen different standards by placing Mn-fibers in seawater spiked with various amounts of ^{227}Ac (with ^{223}Ra in radioactive equilibrium), ^{228}Th (in radioactive equilibrium with ^{232}Th and ^{224}Ra) and ^{226}Ra. We tested for quantitative adsorption of ^{227}Ac and ^{228}Th on the Mn-fibers by: (1) measuring ^{227}Ac and ^{232}Th in the residual solutions after preparing the Mn-fiber standards and (2) monitoring their ^{223}Ra and ^{224}Ra activities over a period of ~100 days. In the residual solutions, the activities of ^{227}Ac and ^{232}Th were $\leq$ 1.0 % and $\leq$ 5.3 %, respectively, of the activities initially added to the Mn-fibers. Our results indicate that Milli-Q water washing of the Mn-fibers is the major source of our observed losses of thorium. Measurements of ^{227}Ac standards over 1½ years indicate a significant decrease of measurable ^{223}Ra with time prohibiting the long-term use of ^{227}Ac Mn-fiber standards. We found the ^{224}Ra efficiency to be independent of the range of ^{227}Ac, ^{228}Th and ^{226}Ra activities on the Mn-fibers standards used. The efficiency determination for ^{223}Ra, however, may be biased in the case of relatively high ^{224}Ra activities due to insufficient correction of chance of coincidence. Thus we suggest using a single ^{227}Ac Mn-fiber standard for the efficiency determination for ^{223}Ra.

Keyword: Radium isotopes, Mn-fiber standards, RaDeCC system, efficiency determination

1. Introduction

Submarine groundwater discharge (SGD) i.e. any flow of water out across the seafloor is now considered as an important process influencing the coastal environment and the ocean's chemical budget (Burnett et al., 2006; Moore, 1996; Moore, 1999). Taniguchi et al. (2002) estimate that the SGD freshwater flux to the oceans amounts to 6 % of the global river water flux. In the Atlantic Ocean a ^{228}Ra balance suggests the total (freshwater plus recirculated seawater) SGD to be up to 80-160% of the river flux entering the Atlantic Ocean (Moore et al., 2008). Submarine groundwater discharge often carries relatively high dissolved matter content, thus even a small SGD flux may have considerable effects on the coastal environment. For instance, outbreaks of harmful algae blooms have been attributed to the nutrient supply associated with SGD (Hwang et al., 2005; Laroche et al., 1997). SGD may also account for a missing source of elements in the oceans like neodymium (Johannesson and Burdige, 2007) and strontium (Basu et al., 2001).

Radium isotopes, in particular the short-lived ^{223}Ra ($T_{½}$ = 11.44 d) and ^{224}Ra ($T_{½}$ = 3.66 d) have been applied as tracers of SGD due to the following: (1) the isotopes have shown to be uniquely associated with SGD (see e.g. Charette and Scholten, 2008; Charette et al., 2003; Krest and Harvey, 2004; Moore, 1999), and their conservative behaviour in saline waters allows the sources and sinks of radium to be well constrained. (2) ^{223}Ra and ^{224}Ra have half-lives comparable to the time scale of water flow and water mixing processes in subterranean estuaries, and (3) a recently introduced measurement technique i.e. the delayed coincidence counting system (RaDeCC) allows for a relatively easy determination of these short-lived radium isotopes (Moore, 2008; Moore and Arnold, 1996).

Determination of radium isotopes typically requires large volume water samples, on the order of 10's to 100's of liters. For ease of sample transport a preconcentration technique is required. As such, water samples are slowly percolated through acrylic fibers coated with manganese oxide (Moore, 1976). At water flow rates of < 1 l/min radium is believed to be quantitatively retained on the Mn-fibers. For measurements using the RaDeCC system the Mn-fiber is connected to a scintillation cell and helium is circulated through the system which carries the daughters of ^{223}Ra and ^{224}Ra, ^{219}Rn ($T_{½}$ = 3.96 sec) and ^{220}Rn ($T_{½}$ = 55.6 sec), respectively, into the cell where these

are measured (for a more detailed description on the measurement technique see Garcia-Solsona et al., 2008; Moore, 2008; Moore and Arnold, 1996)

In order to convert ^{219}Rn and ^{220}Rn count rates into quantitative ^{223}Ra and ^{224}Ra concentrations the efficiency of the RaDeCC system has to be determined. Thus, the efficiency calibration of the RaDeCC system is crucial to ensure good data quality. One method involves the measurements of Mn-fibers with known ^{223}Ra and ^{224}Ra activities. For the preparation of long-shelf live standards, tracer solutions are required in which ^{223}Ra and ^{224}Ra are in radioactive equilibrium with their grand-parent and parent isotopes, i.e. ^{227}Ac ($T_{½}$ = 21.77 y) and ^{228}Th ($T_{½}$ = 1.91 y) (or ^{232}Th, $T_{½} = 1.4 \times 10^{10}$ y, with daughters in equilibrium), respectively. These isotopes have, in contrast to the short half-lives of ^{223}Ra and ^{224}Ra, relatively long half-lives, thus decay correction of the activities on Mn-fibers is limited permitting the standards to be used for several years.

Different techniques have been described for the preparation of the Mn-fiber standards (Dimova et al., 2008; Moore, 2008; Moore and Arnold, 1996). One common step is the use of water spiked with appropriate amounts of ^{227}Ac (for ^{223}Ra) and ^{232}Th (for ^{224}Ra, in equilibrium with ^{228}Th); this water is passed through the Mn-fibers to allow for adsorption of the radionuclides on the Mn-fiber. A potential problem associated with this approach is whether the adsorption of ^{227}Ac and ^{228}Th on the Mn-fiber is quantitative, i.e. no loss occurred during the preparation of the standards. Shaw and Moore (2002) spiked 180 l of seawater with known amounts ^{227}Ac and found a good recovery (~ 95 %) on Mn-fibers. Dimova et al. (2008) describe that in case of the use of de-ionized water as a carrier only ~ 50% of the thorium adsorbs on the Mn-fiber. Much better adsorption efficiency is achieved if filtered seawater is used.

In this study we prepared several Mn-fiber standards and investigated the extent to which ^{227}Ac and ^{232}Th are quantitatively retained on the fibers. We also discuss the influence of the mixtures of tracer solutions on the RaDeCC efficiency determination. This study is part of an IAEA proficiency test that aims to deliver better comparability of ^{223}Ra and ^{224}Ra measurements between different laboratories.

2. Materials

2.1 Tracer solutions

We prepared a ^{232}Th working solution using $Th(NO_3)_4$ (from Pro Labo). For the calibration of this solution two batches consisting each of 6 aliquots spiked with ^{229}Th standard (National Physical Laboratory) were prepared, the first one in January 2007 and the second one in January 2009. The thorium isotopes were purified using chromatographic columns using the Biorad AG1x8 resin (100-200 mesh). Briefly, aliquots of standard solutions in 8 N HNO_3 were poured over the column, the column was rinsed with 3 times the column volume of 8N HNO_3, and thorium was eluted using 8 N HCl. The thorium isotopes were electroplated on stainless steel discs followed by measurements via alpha spectrometry. For the first batch the mean ^{228}Th activity was 23.32 +/- 0.35 dpm/g with a mean ^{228}Th/^{232}Th activity ratio of 0.969 +/- 0.019, for the second the mean ^{228}Th activity was 24.32 +/- 0.55 dpm/g with a mean ^{228}Th/^{232}Th activity ratio of 0.999 +/-0.013. We used the mean of all batches (^{228,232}Th = 23.88 +/- 0.75 dpm/g) as the activity of our working solution.

From an ^{227}Ac tracer solution (AEA Technology) a working solution was prepared having a nominal activity of 20.8 +/- 1.00 dpm/g (reference date 8 November 2007). This nominal activity was verified by measuring ^{227}Th (Mangini and Sonntag, 1977), the daughter of ^{227}Ac in March 2008 (five aliquots) and in January 2009 (six aliquots). We added appropriate amounts of ^{229}Th tracer followed by a purification procedure for thorium as described above. Assuming ^{227}Ac to be in radioactive equilibrium with ^{227}Th the mean activity was 19.43 +/- 0.96 dpm/g for the first batch and 20.02 +/- 0.88 dpm/g for the second batch. In this study we used the average activity of all batches (^{227}Ac = 19.75 +/- 1.00 dpm/g., reference data 8 November 2007).

From a ^{226}Ra reference material (NIST 4957) a working solution of 108 dpm/g was prepared. Mn-fibers were purchased from SCI (Scientific Computer Instruments, South Carolina, US).

2.2 Preparation of Mn-fiber standards

Appropriate amounts of ^{227}Ac, ^{228}Th and ^{226}Ra were added gravimetrically to 500ml Teflon beakers filled with ~ 250ml of radium-free seawater (Table 1). We prepared the radium free-seawater by passing seawater through a Mn-fiber filled column. The pH of the solution in the

beakers was adjusted to pH 7.5-8 using conc. NH_3OH. Approximately 20 g (dry weight) of Mn-fiber was added to each beaker and allowed to soak for a minimum of 24 hours. Thereafter we placed the Mn-fibers in the Mn-fibers holders (hereafter called cartridges). The remaining solution in the Teflon beakers had a pH of ~ 6. This solution was acidified to pH ~ 2 to remove any ^{227}Ac, radium and thorium that may have adsorbed on the walls of the beaker. Next we adjusted the pH of the remaining solution using NH_3OH to pH 7.5-8 and the solution was poured over the Mn-fiber cartridges. The solution which passed through the cartridge was collected; we again noted a drop to pH ~ 6. Once again we adjusted to pH 7.5-8, and poured the solution over the cartridge. In total this procedure was repeated three times. The seawater that remained on the Mn-fiber was removed by pressurized air and combined with the effluent.

The remaining seawater solution was colourless; it was acidified and stored for later determination of the absorption efficiency of ^{227}Ac and ^{232}Th (see below). In order to remove sea salt which might influence later RaDeCC measurements (Sun and Torgersen, 1998) we washed the Mn-fibers with 1 l of Milli-Q water (we checked the quantitative removal of sea salt using refractometer). Using pressurized air the Milli-Q water was removed from the Mn-fiber so that the water content was between 50 and 80 % of the Mn-fiber dry weight. The remaining Milli-Q wash solution was light brown indicating some Mn mobilization from the Mn-fibers. In a later experiment (the Mn-fiber standards S, T, U, V, M_223, Ac_5, Ac_10) we used only 0.5 l of Milli-Q water with pH adjusted to ~ 8 to wash the Mn-fibers. Even in this 0.5 l Milli-Q wash we observed a light brownish colour. We also tested if pre-washing the new Mn-fibers in Milli-Q water (pH ~8) and in seawater would reduce the brownish colour of the Milli-Q wash. Despite this additional precaution a light brownish colour was always observed in the final Milli-Q wash. The Milli-Q wash solution was acidified and stored for later ^{227}Ac and ^{232}Th analyses (see below).

2.3 Measurements of Mn-fiber standards with RaDeCC

For the measurements of the standard Mn-fibers we followed the procedures described in Moore and Arnold (1996) and Moore (2008). Before each measurement the water content of the Mn-fiber standard was determined. If necessary the water content was adjusted to be between 50 and 80% of the Mn-fiber dry weight. We added the appropriate amount of water gravimetrically;

complete flushing of the Mn-fibers with water was avoided. In the beginning of the experiment we added Milli-Q water; later we used radium-free tap water to adjust for the correct water content.

Mn-fiber standards containing only ^{223}Ra or only ^{224}Ra were measured until we reached 600-800 counts in the respective ^{219}Rn and ^{220}Rn windows. Mixed standards, i.e. standards containing both, ^{223}Ra and ^{224}Ra were counted until we obtained 600-800 counts in the ^{220}Rn window and 1000-1200 counts in the total counts window, and these counts where noted. The counting was then continued until we reached ~ 300 counts in the ^{219}Rn window. These different counting periods are necessary in order to minimize the background contribution due to radon (^{222}Rn) daughters, which can contribute significantly to the count rate in the ^{220}Rn and total count windows. This background contribution is negligible for ^{219}Rn. The results of the measurements were corrected for chance of coincidence following Moore and Arnold (1996):

$$\mathrm{corr220} = \mathrm{cpm\,220} - \frac{[(\mathrm{cpm\,total} - \mathrm{cpm\,220} - \mathrm{cpm\,219})^2 \times 0.01]}{\{1 - [(\mathrm{cpm\,total} - \mathrm{cpm\,220} - \mathrm{cpm\,219}) \times 0.01]\}} \quad (1)$$

$$\mathrm{final\ 220} = \mathrm{corr\ 220} - \frac{[(1.6 \times \mathrm{corr\ 219})^2 \times 0.01]}{[1 + ((1.6 \times \mathrm{corr\ 219}) \times 0.01)]} \quad (2)$$

$$\mathrm{corr\ 219} = \mathrm{cpm\,219} - \frac{[(\mathrm{cpm\,total} - \mathrm{corr\ 220} - \mathrm{cpm\,219})^2 \times 0.000093]}{\{1 - [(\mathrm{cpm\,total} - \mathrm{corr\ 220} - \mathrm{cpm\,219}) \times 0.000093]\}} \quad (3)$$

$$\mathrm{final\ 219} = \mathrm{corr\ 219} - (\mathrm{corr\ 220} \times 0.0255) \quad (4)$$

where cpm total, cpm 220 and cpm 219 are the counts per minute in the respective windows and the constants are corrections for cross-talk between the channels.

The measured activities are expressed in efficiency of the respective isotope (eff219 for ^{223}Ra, eff220 for ^{224}Ra; eff total for total counts) i.e. the ratio of the activity measured (final 219, final 220 and total cpm) and the activity that was used to prepare the Mn-fiber standards (dpm $(^{223}\mathrm{Ra})_{\mathrm{stand}}$, dpm $(^{224}\mathrm{Ra})_{\mathrm{stand}}$):

$$\text{eff } 219 = \frac{\text{final } 219}{\text{dpm}(^{223}Ra)_{\text{stand}}} \quad (5)$$

$$\text{eff } 220 = \frac{\text{final } 220}{\text{dpm}(^{224}Ra)_{\text{stand.}}} \quad (6)$$

$$\text{eff total} = \frac{\text{cpm total} - \text{total bkg cpm} - 2 \times 219\,\text{cpm}}{\text{dpm}(^{224}Ra)_{\text{stand}}} \quad (7)$$

Because the efficiency of our two RaDeCC counters differs slightly we measured the Mn-fiber standards always with the same detectors (detector 1 and detector 3) during this study.

2.4 Analyses of ^{227}Ac and ^{232}Th in seawater solution and in Milli-Q wash

In order to determine the fraction of thorium not adsorbed on the Mn-fibers we measured the isotope ^{232}Th in the seawater solution and the Milli-Q wash of Mn-fiber standards A, B, C, G, H, I, J and U. Aliquots (~ 10%) of both, the seawater solution and the Milli-Q wash were removed from those samples for which also ^{227}Ac was determined (i.e. standards C, E, F, G, H and I). The aliquots from standards E and F which have no thorium tracer added were used as blanks. We spiked the seawater and Milli-Q water aliquots with appropriate amounts of ^{229}Th and Fe-solution. To these solutions we added conc. NH_3OH to precipitate ferric hydroxide. The supernatant was siphoned off and the remaining precipitate was dissolved in 8 N HNO_3. Further purification followed the methods described in section 2.1. For aliquots from standards C, E, F, G, H, and I, ^{232}Th was measured using HR-ICPMS (AXIOM). Measurements of ^{232}Th were performed by alpha spectrometry for aliquots from standards A, B, G and U. As the chemical behavior of ^{232}Th and ^{228}Th can be assumed to be the same, we can infer from the ^{232}Th measurements the fraction of ^{228}Th that did not adsorb on the Mn-fibers, i.e. the relative loss of ^{228}Th.

For ^{227}Ac determination in the seawater solution and Milli-Q wash, we developed a new, simple method, which can be summarized as follows: The water samples (150 - 300 ml) were acidified with HCL to pH 1. Samples were spiked using a NIST certified ^{229}Th/^{225}Ac tracer. Actinides from the sample solution were pre-concentrated via lead sulfate co-precipitation (Martin et al., 1995). A commercially available extraction chromatographic column containing N,N,N',N'-tetra-n-octyldiglycolamide (DGA column manufactured by Eichrom, Horwitz et al., 2005) was

chosen for the separation of actinium from other actinides and the sample matrix. We dissolved the lead sulfate precipitate in 20 ml of 4M HCl. In 4 M HCl, the actinides are well retained on the DGA column while radium and other alkaline earth elements have no affinity and pass through the column without retention. To rinse any leftover alkaline earth elements and iron from the column 3M HNO_3 were used. In the next step we eluted actinium with 2 M HCl which recovers Ac but leaves Th and other actinides retained on the DGA column. The procedure was tested using an aliquot of $^{229}Th/^{225}Ac$ certified NIST solution which offered an ideal opportunity to prove good column separation between actinium and thorium. Similar to findings of Horwitz et al. (2005) we found that the presence of iron in the load solution positively affected the actinium uptake on the DGA column and in these test solutions increased the chemical recovery from 50% ($^{229}Th/^{225}Ac$ solution in de-ionized water) to nearly 100 % ($^{229}Th/^{225}Ac$ in de-ionized water with 50 mg Fe). The actinium fraction was prepared for alpha spectrometric measurement via cerium fluoride micro-precipitation (Dulaiova et al., 2001). From the analysis of several standard samples we found very good agreement between our results and certified NIST values. This ^{227}Ac radiochemical separation method showed good chemical recoveries (80±8%, n=14) for both, seawater and Milli-Q solutions. The minimum detectable activities (MDA) of ^{227}Ac using alpha spectrometry were determined to 0.001dpm/sample using an acquisition time of 1 week. The measured samples had ^{227}Ac activities ranging from below the MDA up to 0.1dpm per sample.

3. Results and Discussions

There are two approaches to determine whether the adsorption of the tracers ^{223}Ra, ^{224}Ra, ^{227}Ac, and ^{228}Th was quantitative during the preparation of the Mn-fiber standards: The first option is a continuous monitoring of the activities of the Mn-fibers, the second is the measurements of ^{227}Ac and ^{232}Th in the seawater solution and in the Milli-Q left over from the preparation of the standards.

3.1 Monitoring of Mn-fiber standard activities

If all isotopes present in the tracer solutions were quantitatively adsorbed on the Mn-fiber standards the activities of ^{223}Ra and ^{224}Ra on the Mn-fiber standards and thus eff219 and eff220 should not change over time because they are in radioactive equilibrium with their respective

parent and grand-parent nuclides. In the event that grand-parent and parent nuclides were quantitatively adsorbed whereas radium was lost, eff219 and eff220 would increase with time until parent-daughter radioactive equilibrium is re-established. However, under the experimental conditions of this study adsorption of radium on Mn-fibers should be quantitative (Moore, 2008); thus a loss of radium is not likely. In the case that grand-parent and/or parent nuclides are not quantitatively adsorbed on the Mn-fibers eff219 (^{223}Ra) and eff220 (^{224}Ra) will decrease over time.

We can predict possible changes of ^{223}Ra and ^{224}Ra by solving the serial decay equations (8) and by applying different loss fractions, i.e. less than quantitative adsorption of grand-parent (^{227}Ac) and parent (^{227}Th, ^{228}Th) isotopes:

$$\frac{dN_i}{dt} = -\lambda_i N_i + \lambda_{i-1} N_{i-1} \qquad (8)$$

where $\frac{dN_i}{dt}$ is the activity of the daughter nuclide at time t, $-\lambda_i N_i$ is the decay of nuclide N_i, and $\lambda_{i-1} N_{i-1}$ is the in-growth of N_i by decay of the parent nuclide N_{i-1}.

The activity of ^{228}Th, ultimately determines the activity of ^{224}Ra on the Mn-fibers. As shown in Fig. 1 with increasing loss of ^{228}Th the activity of ^{224}Ra will decrease accordingly. For example, in the case of a 10% loss of ^{228}Th the ^{224}Ra activity will decrease by 5% after ~ 20 days. The parent ^{227}Th ($T_{½}$ = 18.7 d) and grand-parent ^{227}Ac ($T_{½}$ = 21.77 y) control ^{223}Ra activities: each may have different adsorption efficiencies on the Mn-fibers. Thus, variable losses of ^{227}Ac and of ^{227}Th are possible. In Fig. 2 we allow for different combinations of ^{227}Ac and/or of ^{227}Th loss the resulting change of ^{223}Ra activity on the Mn-fiber over time. Assuming a 20% loss of ^{227}Ac (Fig. 2a) and no loss of ^{227}Th the ^{223}Ra activity will decrease by ~ 5% after 20 days. When both are not retained quantitatively the relative decline in the ^{223}Ra activity is much faster during the first ~ 20 days, especially if a significant amount of ^{227}Th is lost (Figs. 2b-c). If we assume no loss of ^{227}Ac but a loss of ^{227}Th the ^{223}Ra activity will decrease in the first ~ 20 days but radioactive equilibrium between all three isotopes will be re-established after ~ 100 days (Fig. 2d).

We monitored eff219 and ef220 determined from Mn-fiber standards A - C, E - J for ~ 100 days starting from the day the standards were prepared (Fig. 3). Less frequent measurements were conducted for standards D, U, M_223, Ac_5 and Ac_10. The plots of eff219 and eff220 over time show some scatter with no clear trend (Fig. 3) We evaluated these monitoring data more rigorously by comparing average RaDDeC counting efficiencies determined during the first ~ 10 days after preparation with those measured after ~ 50 days (Tab. 2). We observe a mean decrease of 11.9 +/- 8.7 % for eff219 between the two measurement periods whereas there is little or no change for mean eff220 (3.9 +/- 4.4 %.). However, except for standards A and E all the changes in the observed efficiencies are associated with high uncertainties i.e. the relative efficiency changes are in the same range as their 2σ uncertainty levels (Tab. 2). Thus, apart from Mn-fibers standards A and E we cannot detect in the first 100 days any changes in the activities of the standards within the precision of our measurements.

3.2 ^{227}Ac and ^{232}Th in seawater solution and in Milli-Q wash

In table 3 the activities of ^{227}Ac and ^{232}Th measured in the seawater solution and in the Milli-Q wash are shown. For standard G we found the highest loss of ^{232}Th, which in total (combined activities in seawater solution and Milli-Q wash) amounts to 5.3% of the initial ^{232}Th activity added to the Mn-fiber standard (Fig. 4). This is the thorium that was not adsorbed on the Mn-fiber, i.e. it was lost during one of the steps of standard preparation. Thus, the exact ^{228}Th activity on the Mn-fiber G (and that of ^{224}Ra after radioactive equilibrium is re-established) is 5.3 % lower (Table. 3). For the other Mn-fiber standards the loss of ^{232}Th is $\leq$ 3%. Apart from standard G most ^{232}Th is lost when washing the Mn-fibers with Milli-Q water. This is most likely due to the relatively low pH of Milli-Q which probably causes some removal of MnO_2 from the Mn-fibers. Although we adjusted the pH before the Milli-Q was poured over the Mn-fibers the lack of a buffering capacity of Milli-Q will quickly lower the pH of Milli-Q once it gets in contact with the Mn-fibers. As seen in the case of standard U, the loss of ^{232}Th during the Milli-Q wash can be minimized if the volume of the wash is reduced.

The activities of ^{227}Ac in the seawater solution and in the Milli-Q wash are generally $\leq$1.0 % of the initial ^{227}Ac activity added to the standards (Table 3). For Mn-fiber standards S and T for which washing with Milli-Q water was further reduced the loss of ^{227}Ac amounts to only 0.1% of

the initially added ^{227}Ac. Thus the adsorption of ^{227}Ac on these Mn-fibers is nearly quantitative under these experimental conditions. It should be noted that, if ^{227}Ac is quantitatively adsorbed, the ^{223}Ra activity on the Mn-fibers may change over time in the case of ^{227}Th loss (see section 3.1) (Fig. 2d). If we assume a 5% loss of thorium, the ^{223}Ra activity will decrease by 2.5% after 20 days following the preparation of the standard, and will later increase until radioactive equilibrium is achieved. However, such changes in the activities are difficult to resolve within measurement uncertainties using the RaDeCC system.

One conclusion from the monitoring of efficiencies and from the measurements of ^{232}Th and ^{227}Ac in the wash solutions is that the latter approach gives far more precise information on how much of the tracers did not adsorb quantitatively on the Mn-fibers (due to the better precision of ICPMS and alpha spectrometry). With this information the activities on the Mn-fiber standards can be corrected (Table 3) and thus can still be used for efficiency determination of the RaDeCC system. Monitoring the activities of the Mn-fiber standards gives more qualitative information on whether or not tracers are fully adsorbed, but only in those cases where the loss of tracer is significantly higher than the uncertainty of the RaDeCC measurements. According to Garcia-Solsona et al. (2008) relative uncertainties for ^{223}Ra and ^{224}Ra RaDeCC measurements are at best 7% and 4%, respectively for samples with high activities (> 10 dpm); for samples with lower activities minimal uncertainties are 12% and 7% for ^{223}Ra and ^{224}Ra, respectively. Such uncertainties do not permit a proper correction of Mn-fiber standards for the loss of tracer activities, as this correction would induce relatively high uncertainties in the efficiency determination of the RaDeCC system which would in turn propagate to the measurements of unknown samples.

3.3 The decrease in eff219

For all Mn-fibers we observed a decrease over time in the eff219 (Table 2). As discussed above the average decline is within the statistical uncertainties of the measurements. However, for standards E with high ^{223}Ra (10.2 dpm) we obtained better counting statistics, and we measured a significant decline of 11.8 +/- 3.7 % despite an insignificant loss of tracer during the preparation of this standard (Table 3).

This phenomenon was also observed for standards S and T which have been repeatedly used to check the efficiency of our RaDeCC detectors over the past 1½ years. In this period we observed a clear decrease in eff219 by 32.8 +/- 6.7 % and 26.6 +/- 7.1 for standards S and T, respectively (Fig. 5). As eff220 remained relatively constant over the same period, changes in detector performance cannot explain the decrease in eff219. We prepared additional ^{227}Ac standards (M_223, prepared 21 May 2009; Ac_5 and Ac_10, both prepared 20 June 2009) which resulted in eff219 in between 0.41 and 0.43 (Fig. 5, Table2). The eff219 determined from these new standards confirms that eff219 for our systems did not change considerably.

In order to test whether unevenly distributed moisture was the cause for the apparent decline in eff219, standards S and T were re-wetted several times. Further, we fluffed the fiber, and standard S was flushed with Milli-Q water. However, none of these procedures changed eff219 determined from standards S and T. In order to verify the activity of ^{223}Ra, the Mn-fiber standards S and T were ashed; and ^{223}Ra measurements by gamma spectrometry (Charette et al., 2001) revealed a ^{223}Ra activity of 20.9 +/- 1.2 dpm and 21.5 +/- 1.4 dpm for standards S and T respectively (reference date July 2009). This activity is similar to the one originally adsorbed on standards S and T (^{223}Ra = 19.6 +/- 1.0 dpm; reference date October 2009). Thus we have no indication for a loss of ^{223}Ra during the long-term handling and usage of these standards. In order to study if frequent measurements of Mn-fibers and/or adding of water (to adjust the moisture content of the Mn-fibers) can cause a decrease in eff219 we prepared Mn-fiber standard V (Table 1). After the first measurement standard V was sealed (to prevent drying of Mn-fiber), and measured again after 153 days; and these measurements resulted in 17.2 % lower eff219 compared to the first measurement (Table 2, Fig. 5).

As the half-lives of ^{223}Ra and ^{224}Ra daughters ^{219}Rn ($T_{½}$ = 4.0 s) and ^{220}Rn ($T_{½}$ = 55.6 s) are the only difference in the RaDeCC measurement procedure (note that any changes in the detector system would affect both, ^{219}Rn and ^{220}Rn), a possible explanation for the drop in eff219 is a decrease in the transfer rate of radon from the Mn-fibers into the helium stream. The half-life of ^{219}Rn is significantly shorter than that of ^{220}Rn. Hence, if the surface structure of the Mn-fibers changes so that the transfer rate of radon from the Mn-fibers to the helium stream would be slowed-down sufficiently ^{219}Rn would decay significantly but not ^{220}Rn. This would lead to a

decrease in the measurable ^{219}Rn and thus in eff219. We can only speculate about the cause for this decrease in eff219. For instance, recrystallization of amorphous Mn-phases into Mn-oxides may have the potential to change the surface structure of Mn-fibers. The consequence is that standards for ^{223}Ra efficiency calibrations can be used only for a limited time.

3.4 Are there "ideal" activities of Mn-fiber standards for efficiency determinations?

We selected the range of activities of the Mn-fiber standards so that they resemble the activities of natural samples; and this range was complemented by single standards (standards E, F, G, S, T, and U) with relatively high activities. The resulting efficiencies for our detectors including a correction for the loss of tracers (where applicable) are shown in Figure 7 (note that we used only eff219 obtained within the first ~ 10 days after preparation of the standards). The ^{223}Ra efficiencies range between 0.41 and 0.49. For standard D we arrive at a higher efficiency of 0.60. The reason for this "outlier" will be discussed in more detail below. Neglecting this outlier the average ^{223}Ra efficiencies for our detectors 1 and 3 are 0.46 +/- 0.02 and 0.43 +/- 0.03, respectively. The ^{224}Ra efficiencies (range 0.57 - 0.60) are in good agreement between the various Mn-fiber standards (Fig. 6) (average for detector 1: 0.58 +/- 0.01; average for detector 3: 0.58 +/- 0.02). The same holds for the efficiencies for ^{224}Ra calculated based on total counts (average detector 1: 1.36 +/- 0.01; average detector 3: 1.35 +/- 0.03). We obtain this good agreement in the ^{224}Ra efficiencies although we used variable mixtures and variable activities of ^{223}Ra, ^{224}Ra and ^{226}Ra on the Mn-fiber standards. Thus, we did not observe the range of tracer activities and mixtures to influence the ^{224}Ra efficiency determination.

3.4.1 Influence of chance of coincidence correction on ^{223}Ra efficiency determination

The measurements of Mn-fiber standard D give significantly higher comparable efficiency for ^{223}Ra. This Mn-fiber standard differs from the others in that it has comparatively higher ^{228}Th (Table.1). During RaDeCC counting some of the counts that should only be registered in the 220 window, also appear in the 219 window. This cross-talk between the channels is corrected by applying the chance of coincidence correction (see equations 1-4). In order to evaluate how this correction influences our efficiency determinations we measured a series of Mn-fibers having different ^{224}Ra activities but no ^{223}Ra. For (chance of coincidence corrected) final220 < 7 cpm

the final219 is on average 0.03 +/- 0.03 cpm (n = 32), but for final220 $\geq$ ~7 cpm the final219 increases significantly (Fig. 7). Thus in cases of a high final220 count rate (> 7cpm) the final219 count rate will be biased (too high). The apparently high eff219 we derived from Mn-fiber standard D can be attributed to insufficient chance of coincidence correction.

This insufficient correction influences the ^{223}Ra efficiency determination when using mixed Mn-fiber standards. For instance, the mixed standards I and J have ^{224}Ra ~ 9.6 dpm and ^{223}Ra ~ 1.05 dpm. Such a ^{223}Ra activity results in approximately final219 of ~ 0.4 cpm. We can estimate the fraction of final219 counts which derive from insufficient chance of coincidence correction from measurements of single Mn-fiber standards G (^{224}Ra =11.1 dpm; corrected for loss). For standards G we find a final219 = 0.042 +/- 0.063 cpm (n= 13). Thus the insufficient chance of coincidence correction can account for about ~ 10% of the final219 counts in standards I and J and cause the comparable higher ^{223}Ra efficiencies we obtained from standards I and J (Table 2). In order to avoid the influence of insufficient chance of coincidence correction single-tracer standards are preferable for ^{223}Ra efficiency determinations.

In field samples having relatively high ^{224}Ra (> 7cpm) the insufficient chance of coincidence correction will hamper a precise ^{223}Ra determination. In order to minimize this problem we normally wait for some decay of ^{224}Ra. After 8 days ~ 75 % of ^{224}Ra but only 35% of the ^{223}Ra has decayed (Moore, 2008) so that the cross-talk between the 219 and 220 windows is minimized. Lower ^{224}Ra also allows for longer counting periods and thus better ^{223}Ra counting statistics.

4. Conclusion

We prepared seventeen Mn-fiber standards for efficiency calibration of the delayed coincidence counting system (RaDeCC) for measurements of ^{223}Ra and ^{224}Ra. These standards were made by letting Mn-fiber soak in seawater for a minimum of 24 h. This seawater had been spiked with variable amounts of ^{227}Ac, ^{232}Th and ^{226}Ra tracer solutions with daughters in radioactive equilibrium (except for ^{226}Ra). In order to assess the quantitative adsorption of the tracers on the Mn-fibers we took two approaches: (1) monitoring of the activities (^{223}Ra and ^{224}Ra) of Mn-fiber standards for ~ 100 days and (2) measurements of ^{227}Ac and ^{232}Th (in equilibrium with ^{228}Th) in

seawater and in Milli-Q solutions left over from the preparation of the Mn-fiber standards. In the monitoring experiment we compared the activities determined during the ~ first 10 days after the preparation of the Mn-fiber standards with those measured after 50 days. For all the standards the activities determined for these periods differ on average by 11.9 +/- 8.7 % for ^{223}Ra and by 3.9 +/- 4.4 % for ^{224}Ra. In each case, the seawater and in the Milli-Q wash solutions concentrations of ^{227}Ac and ^{228}Th were at most 1.0 % and 5.3%, respectively, of the total activity initially added to the Mn-fiber standards. We observed that washing of the Mn-fiber with Milli-Q water to remove sea salt was the step where most of the thorium loss can occur. Reducing the volume of the Milli-Q wash from 1 l to 0.5 l reduced the loss of thorium to $\leq$ 1%. Measurements of thorium and ^{227}Ac in the residues leftover from the preparation of the Mn-fiber standards give more precise results on possible losses of tracers when compared to RaDeCC analysis of the Mn-fiber, and thus are an essential step to assure the quality of the standards.

We observed a significant decrease in the measurable ^{223}Ra activity on the Mn-fibers over a period of 1½ years which we attribute to a reduction in the radon transfer rate from the Mn-fibers to the helium stream of the RaDeCC system. This change of the Mn-fiber performance hampers the long-term use of ^{227}Ac Mn-fiber standards for efficiency calibration. However, once eff219 is determined using a newly prepared standard there is no need for frequent reassessment of eff219 as long as eff220 remains constant. For field samples the decrease in the measurable ^{223}Ra may have an effect on the supported ^{223}Ra determination (^{227}Ac) as these measurements are normally performed ~ 3 month after sampling.

The efficiency determination for ^{224}Ra is neither influenced by the range of activities on Mn-fibers standards nor if single ^{224}Ra and/or mixtures of ^{223}Ra, ^{224}Ra and ^{226}Ra were used. For the efficiency determination of ^{223}Ra, however, we observed an influence of the ^{224}Ra activities for final220 > 7 cpm which is caused by insufficient chance of coincidence correction. Thus for the ^{223}Ra efficiency determination we recommend the use of single tracer Mn-fiber standards with relative high ^{227}Ac activities.

Acknowledgements

This study was stimulated by the “Workshop on the measurement of short-lived radium isotopes using the RaDeCC delayed coincidence technique”, Monaco2006. We thank W. Moore and B. Burnett for their comments on an early version of this manuscript. I. Levy is acknowledged for her assistance in the laboratory. M. Charette and H. Dulaiova were supported by a grant from the National Science Foundation (OCE- 0751461). The International Atomic Energy Agency is grateful for the support provided to its Marine Laboratories by the Government of the Principality of Monaco.

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Figure captions

Figure 1: Model of changes of ^{224}Ra activities over time for different theoretical losses of ^{228}Th.

Figure 2: Model of changes of ^{223}Ra activities over time for different theoretical losses of ^{227}Ac and ^{227}Th.

Figure 3: Monitoring of eff219 and eff220 for the different Mn-fibers standards. A clear trend of efficiency change over time is not obvious.

Figure 4: Relative amount of ^{232}Th found in the excess seawater and Milli-Q water that was not adsorbed on the Mn-fibers

Figure 5: Change of eff219 determined from standards S and T over time (^{227}Ac decay corrected). The eff220 determined from standard U standard did not change in the same period suggesting that changes in the detector efficiencies cannot explain the observed decrease in eff219.

Figure 6: Efficiencies for ^{223}Ra and ^{224}Ra for several Mn-fiber standards. The activities on the Mn-fibers were corrected for the loss of tracers (where applicable); for ^{223}Ra only the data obtained during the first 10 days were used. Efficiencies for Detectors 1 and 3 are mean efficiencies based on all Mn-fiber standards.

Figure 7: Final 220 counts (chance coincidence corrected counts) versus final 219 counts (chance coincidence corrected); for final 220 counts $\geq$ ~ 7cpm insufficient chance coincidence correction significantly biases the 219 count rate. This experiment was performed using detectors in two labs (WHOI, IAEA-Monaco).

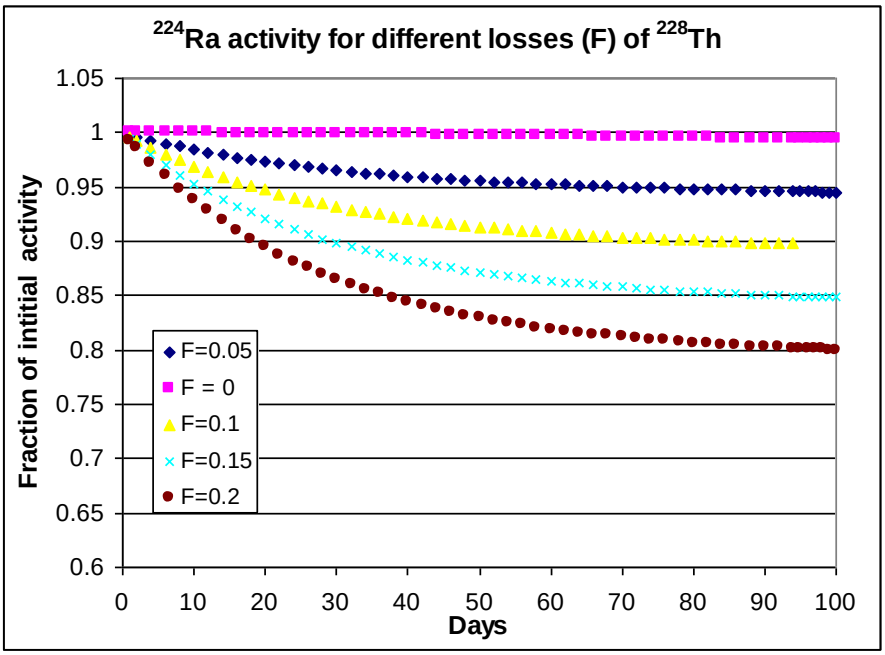

224Ra activity for different losses (F) of 228Th
Fraction of intitial activity
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0
10
20
30
40
50
60
70
80
90
100
Days
F=0.05
F = 0
F=0.1
F=0.15
F=0.2

Figure 1:

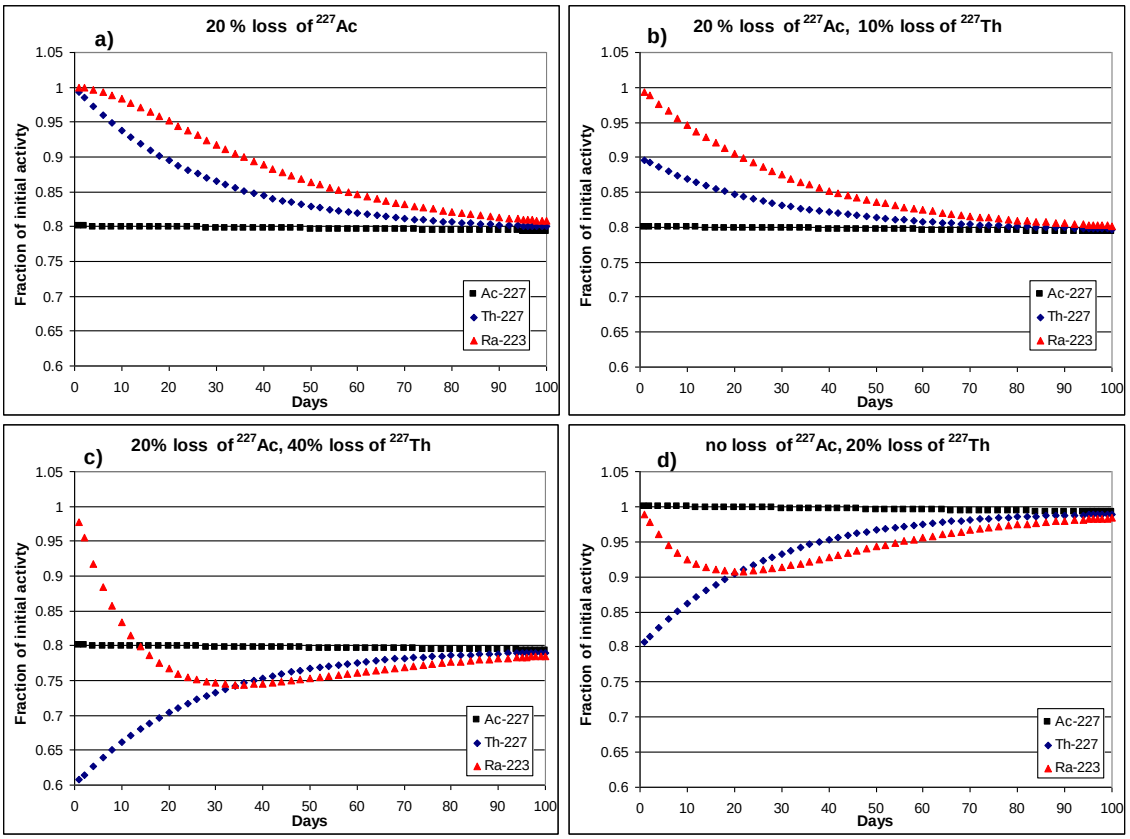

a)
20 % loss of 227Ac
b)
20 % loss of 227Ac, 10% loss of 227Th
c)
20% loss of 227Ac, 40% loss of 227Th
d)
no loss of 227Ac, 20% loss of 227Th
Fraction of initial activty
Days
Ac-227
Th-227
Ra-223

Figure 2:

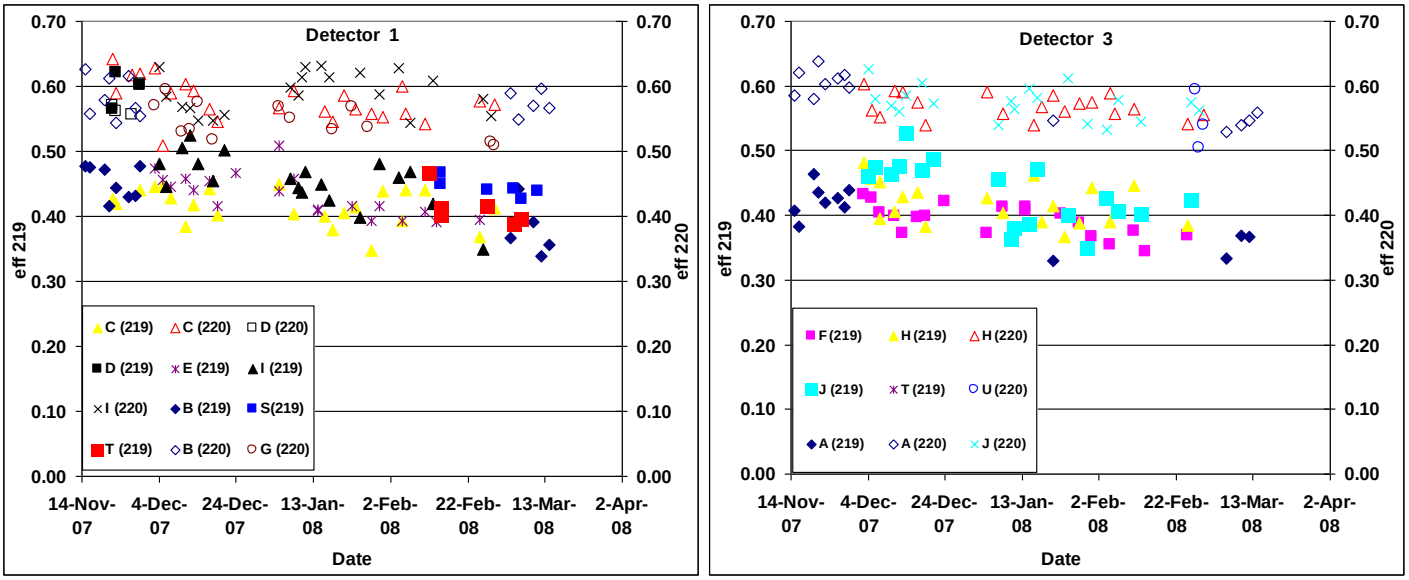


Figure 3:

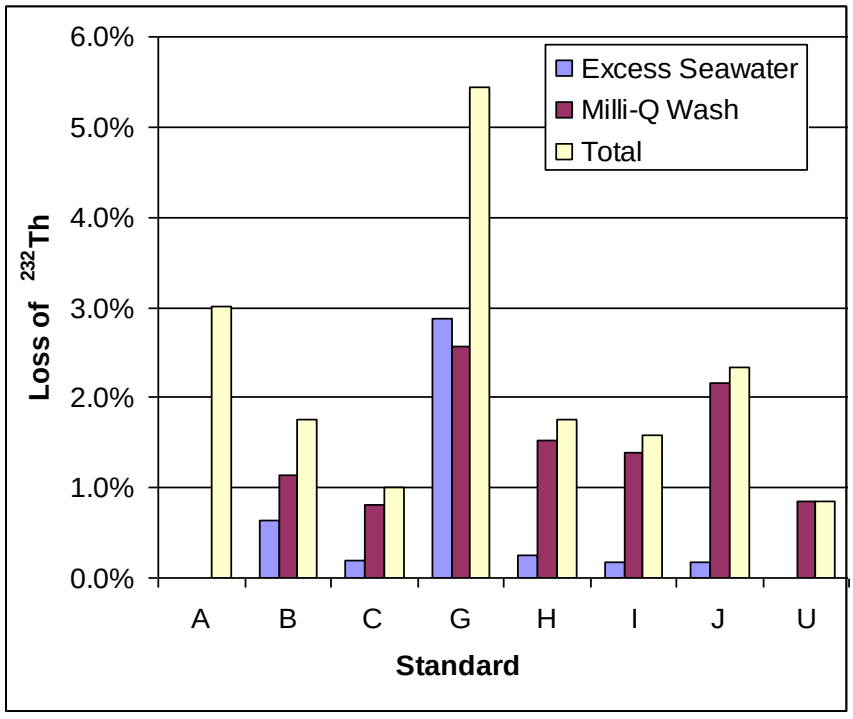


Figure 4:

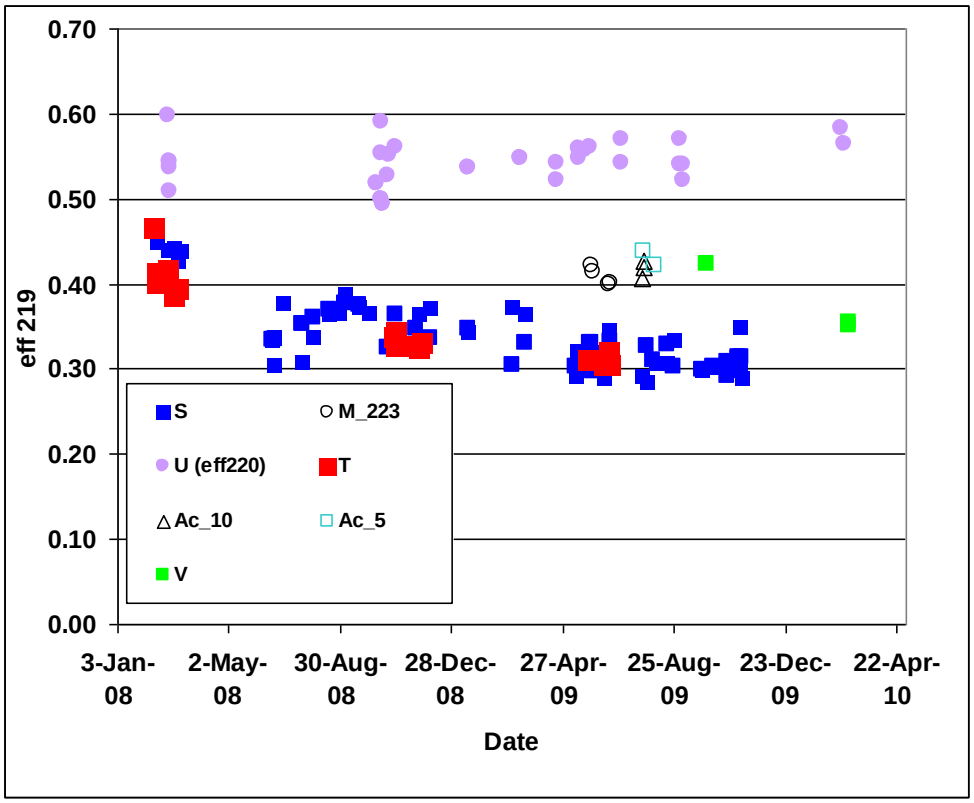
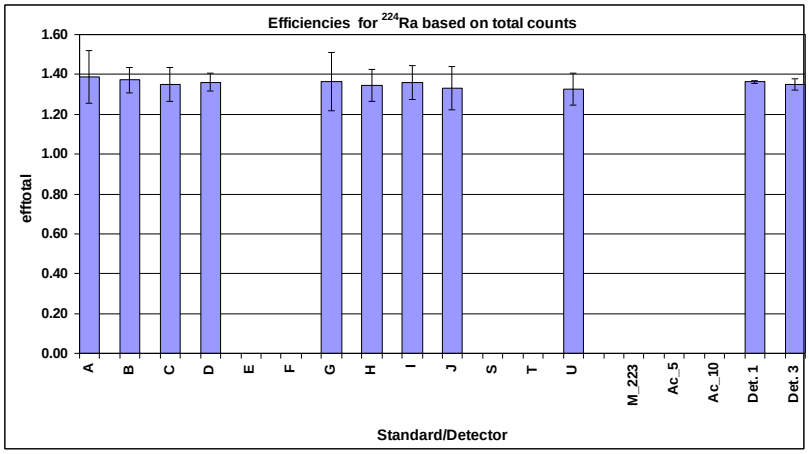

0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
eff 219
S
M_223
U (eff220)
T
Ac_10
Ac_5
V
3-Jan-08
2-May-08
30-Aug-08
28-Dec-08
27-Apr-09
25-Aug-09
23-Dec-09
22-Apr-10
Date

Figure 5:

1

2



3

4 Figure 6:

5

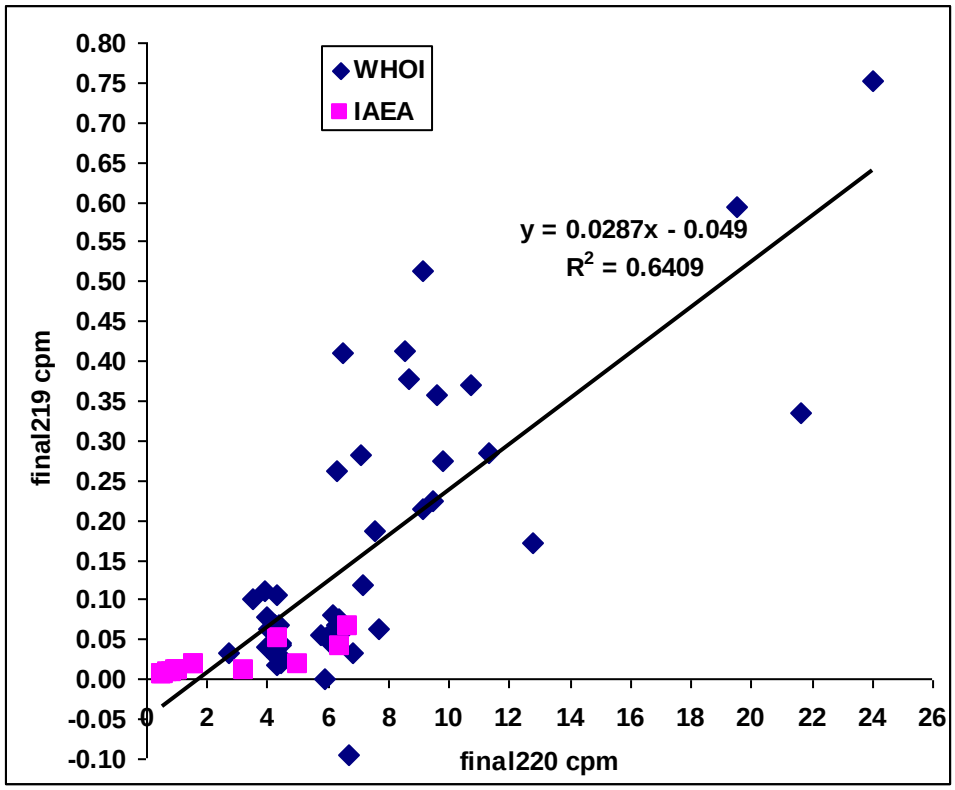

WHOI
IAEA
y = 0.0287x - 0.049
R2 = 0.6409
final219 cpm
final220 cpm
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
0
2
4
6
8
10
12
14
16
18
20
22
24
26

Figure 7:

Mn-Fiber Standard	Date of Preparation	^{223}Ra	^{224}Ra	^{226}Ra
		dpm	dpm	dpm
A	2007-11-14	2.19	6.24	40
B	2007-11-14	2.10	12.1	9.08
C	2007-11-21	2.31	14.8	22
D	2007-11-21	2.11	24.4	22.8
E	2007-12-03	10.3	-	-
F	2007-12-03	10.2	-	-
G	2007-12-03	-	-	-
H	2007-12-03	2.11	14.7	23.0
I	2007-12-03	1.05	9.80	22.7
J	2007-12-03	1.05	9.80	22.9
S	2008-02-11	20.6	-	-
T	2008-02-11	21.6	-	-
U	2008-02-26	-	12.2	-
V	2009-09-28	-	10.0	-
M_223	2009-05-21	20.3	-	-
Ac_5	2009-07-20	4.71	-	-
Ac_10	2009-7-20	9.46	-	-

Table 1: Activities of tracers used for the preparation of the Mn-fiber standards

Mn-Fiber Standard	^{223}Ra first ~ 10 days eff219	+/-	N	^{223}Ra after ~ 50 days eff219	+/-	N	Change %	+/-	^{224}Ra first ~ 10 days eff220	+/-	N	^{224}Ra after ~ 50 days eff20	+/-	N	Change %	+/-
A	0.42	0.03	6	0.35	0.02	6	16.6	7.9	0.61	0.02	6	0.54	0.01	6	10.3	4.0
B	0.45	0.03	6	0.38	0.04	5	16.2	10.6	0.59	0.03	6	0.57	0.02	8	2.5	6.6
C	0.43	0.01	4	0.41	0.04	8	6.0	8.5	0.62	0.02	5	0.57	0.03	8	7.9	5.7
D	0.60	0.03	3						0.57	0.02	3					
E	0.46	0.01	13	0.40	0.01	7	11.8	3.7								
F	0.41	0.02	5	0.36	0.01	5	11.0	6.7								
G									0.56	0.03	5	0.56	0.03	4	-0.2	6.8
H	0.44	0.03	6	0.41	0.03	6	5.2	10.1	0.58	0.02	6	0.56	0.02	6	2.9	4.7
I	0.49	0.03	13	0.44	0.05	6	10.6	11.7	0.58	0.03	5	0.59	0.03	7	-1.7	7.7
J	0.48	0.03	5	0.41	0.03	6	15.5	8.5	0.58	0.04	7	0.56	0.02	6	4.9	5.4
S	0.45	0.02	4	0.31[a)]	0.02	5	32.8	6.7								
T	0.42	0.03	4	0.31[b)]	0.01	3	26.6	7.1								
U									0.55	0.05	3					
V	0.42	0.02	1	0.35[c)]	0.02	2	17.2	5.0								
M_223	0.41	0.01	4													
Ac_5	0.43	0.01	4													
Ac_10	0.41	0.03	3													
Mean	0.44	0.03		0.39[d)]	0.03		11.9[d)]	8.7	0.58	0.02		0.57	0.01		3.9	4.4

a) eff219 in October/November 2009; b) eff219 in Mai/June 2009; c) eff219 in April 2010 d) excluding standards S,T and V

Table 2: Comparison of eff219 and eff220 determined within the first~ 10 days after preparation of standards and after ~ 50 days

Mn-Fiber Standard	^{232}Th in excess seawater	Loss	^{232}Th in Milli-Q	Loss	Total loss	^{232}Th corrected	^{227}Ac in excess seawater	^{227}Ac in Milli-Q	Total loss	^{227}Ac corrected
	dpm	%	(dpm)	%	%	(dpm)	(dpm)	(dpm)	%	(dpm)
A	- [a]		- [a]		3.0 [b]	6.06	n.a.	n.a	-	-
B	0.074 [b]	0.6	0.132 [b]	1.1	1.8	11.9	n.a	n.a	-	-
C	0.0267	0.2	0.115	0.8	1	14.6	n.a	n.a	-	-
E	-	-	-	-	-		<MDA	0.100	1.0	10.2
F	-	-	-	-	-		<MDA	0.076	0.8	10.1
G	0.326 (0.312) [b]	2.8	0.291 (0.292) [b]	2.5	5.3	11.1	-	-		
H	0.0350	0.2	0.217	1.5	1.7	14.5	0.001	n.a	0.1	2.11
I	0.017	0.2	0.132	1.4	1.6	9.64	0.006	n.a	0.6	1.05
J	0.0162	0.2	0.206	2.2	2.3	9.59	<MDA	n.a	-	
S	-	-	-	-	-		0.007	0.029	0.1	20.7
T	-	-	-	-	-		<MDA	0.043	0.2	20.6
U	<MDA [b]		0.100 [b]	0.9	0.9	12.09	-	-	-	

Table 3: ^{232}Th and ^{227}Ac activities found in seawater solution and Milli-Q wash. All activities are indicated in dpm/sample. The relative loss relates the activity measured to the activity used to prepare the Mn-Fiber standards (Tab. 1). a) left-over seawater and left-over Milli-Q water were pooled; b) measurement by means of alpha spectrometer; MDA = minimum detectable activities